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Kinetics of HMX and CP Decomposition and Their Extrapolation for Lifetime Assessment*

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Accelerated aging tests play an important role in assessing the lifetime of manufactured products. There are two basic approaches to lifetime qualification. One tests a product to failure over range of accelerated conditions to calibrate a model, which is then used to calculate the failure time for conditions of use. A second approach is to test a component to a lifetime-equivalent dose (thermal or radiation) to see if it still functions to specification. Both methods have their advantages and limitations.

A disadvantage of the 2nd method is that one does not know how close one is to incipient failure. This limitation can be mitigated by testing to some higher level of dose as a safety margin, but having a predictive model of failure via the 1st approach provides an additional measure of confidence. Even so, proper calibration of a failure model is non-trivial, and the extrapolated failure predictions are only as good as the model and the quality of the calibration.

This paper outlines results for predicting the potential failure point of a system involving a mixture of two energetic materials, HMX (nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and CP (2-(5-cyanotetrazolato) pentaammine cobalt (III) perchlorate). Global chemical kinetic models for the two materials individually and as a mixture are developed and calibrated from a variety of experiments. These include traditional thermal analysis experiments run on time scales from hours to a couple days, detonator aging experiments with exposures up to 50 months, and sealed-tube aging experiments for up to 5 years.

Decomposition kinetics are determined for HMX (nitramine octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and CP (2-(5-cyanotetrazolato) pentaammine cobalt (III) perchlorate) separately and together. For high levels of thermal stress, the two materials decompose faster as a mixture than individually. This effect is observed both in high-temperature thermal analysis experiments and in long-term thermal aging experiments. An Arrhenius plot of the 10% level of HMX decomposition by itself from a diverse set of experiments is linear from 120 to 260 °C, with an apparent activation energy of 165 kJ/mol. Similar but less extensive thermal analysis data for the mixture suggests a slightly lower activation energy for the mixture, and an analogous extrapolation is consistent with the amount of gas observed in the long-term detonator aging experiments, which is about 30 times greater than expected from HMX by itself for 50 months at 100 °C. Even with this acceleration, however, it would take ~10,000 years to achieve 10% decomposition at ~30 °C. Correspondingly, negligible decomposition is predicted by this kinetic model for a few decades aging at temperatures slightly above ambient. This prediction is consistent with additional sealed-tube aging experiments at 100-120 °C, which are estimated to have an effective thermal dose greater than that from decades of exposure to temperatures slightly above ambient.

More complete versions of this work (same authors and title) are:

1. LLNL report UCRL-TR-208411 (Nov, 2004).
2. LLNL report UCRL-CONF-210589 (March, 2005), 36th Annual Conf. of the ICT.

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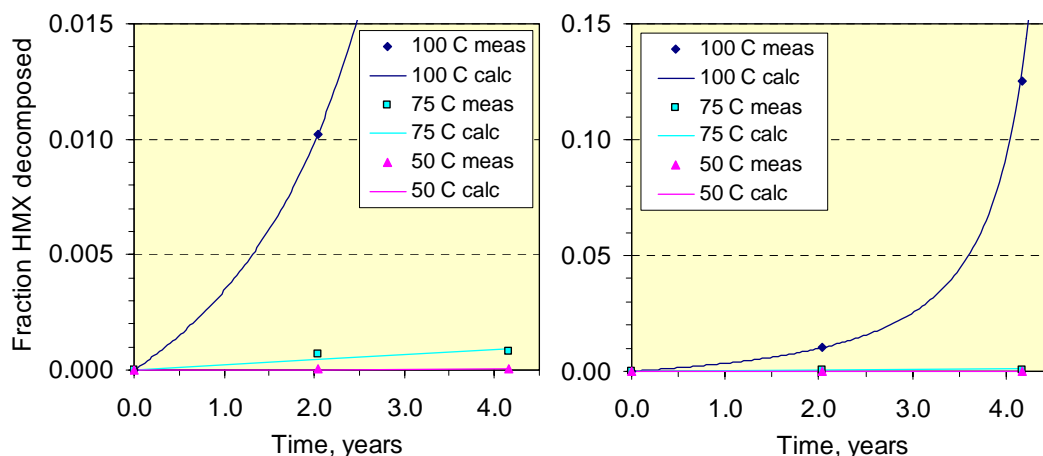


Figure 1. Observed and calculated fractions of HMX decomposed for a fit of an extended Prout-Tompkins nucleation-growth model to the Sandia detonator aging studies. Two scales are shown for a better view of the comparison between experiment and calculation. The acceleratory nature of reaction causes it to be nearly complete by 5 years at 100 °C.

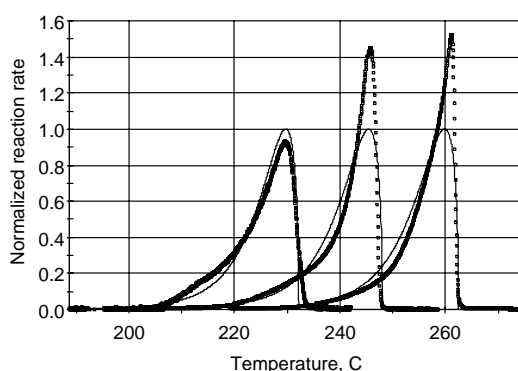


Figure 2. Comparison of model (lines) and experiment (points) for DSC heat release in a hermetically sealed pan at heating rates of 0.1, 0.35, and 1.0 °C/min.

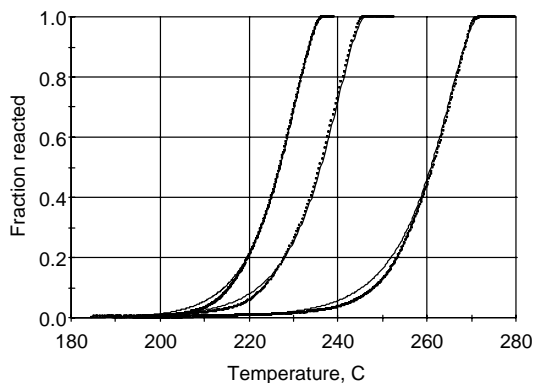


Figure 3. Comparison of model and experiment for weight loss (open-pan TGA) at heating rates of 0.1, 0.2, and 1.0 °C/min, from left to right, respectively. The thin line is the model.

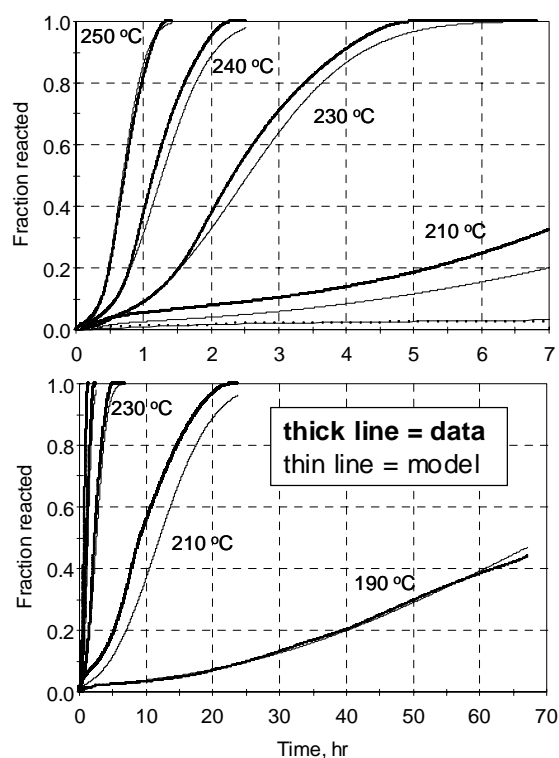


Figure 4. Comparison of model calculations for isothermal weight loss from HMX (open-pan TGA). Two time scales are shown enable a comparison over the entire temperature range. Only partial reaction was achieved at 190 °C due to the slowness of the reaction. The autocatalytic character is particularly evident at the lower temperatures where it is clearly separated from thermal heatup.

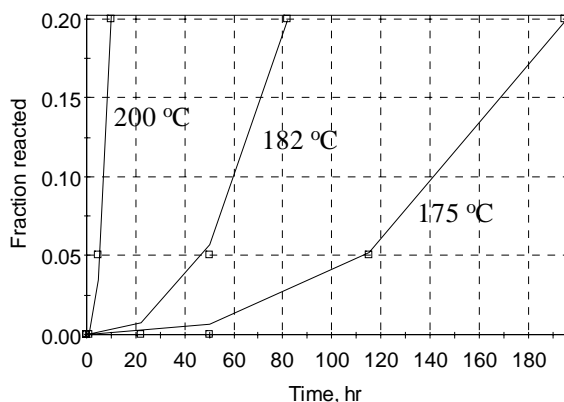


Figure 5. Extended Prout-Tompkins autocatalytic model for the low temperature HMX decomposition data of Behrens and Bulusu at SNL.

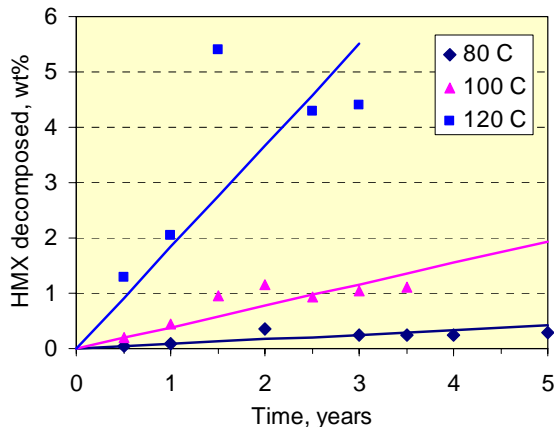


Figure 6. N_2O gas yields as a function of time from long-term HMX decomposition experiments at SNL. Based on an analogy to the more complete product analysis in other experiments, the amount of mass loss from HMX would be only half as great.

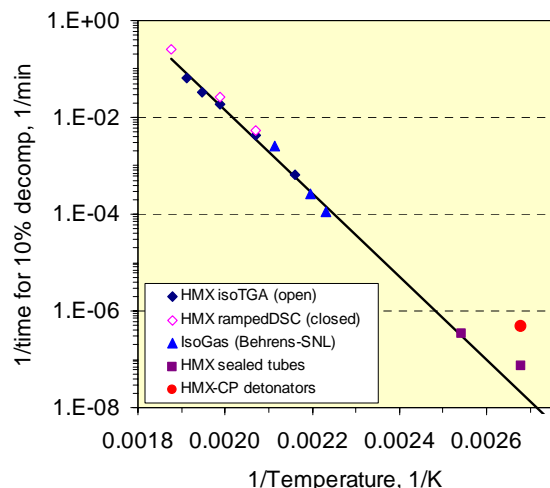


Figure 7. Compilation of rate constants for HMX decomposition from a variety of experiments. Rate constants are expressed in terms of the reciprocal time needed for 10% decomposition. The filled squares for the sealed-tube experiments represent a most likely value based on estimated mass loss.

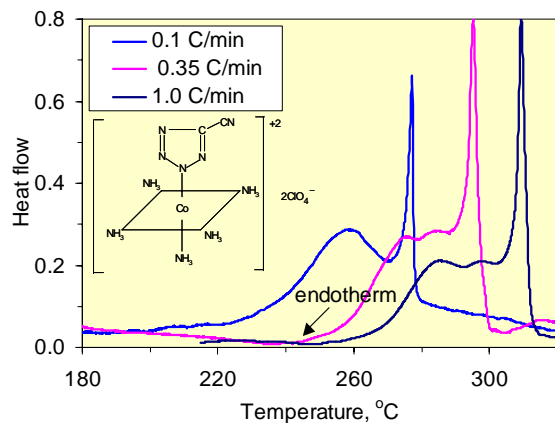


Figure 8. Reaction profiles for decomposition of CP by itself. The first stage of decomposition gives the endotherm most evident for 0.35 °C/min at 240 °C.

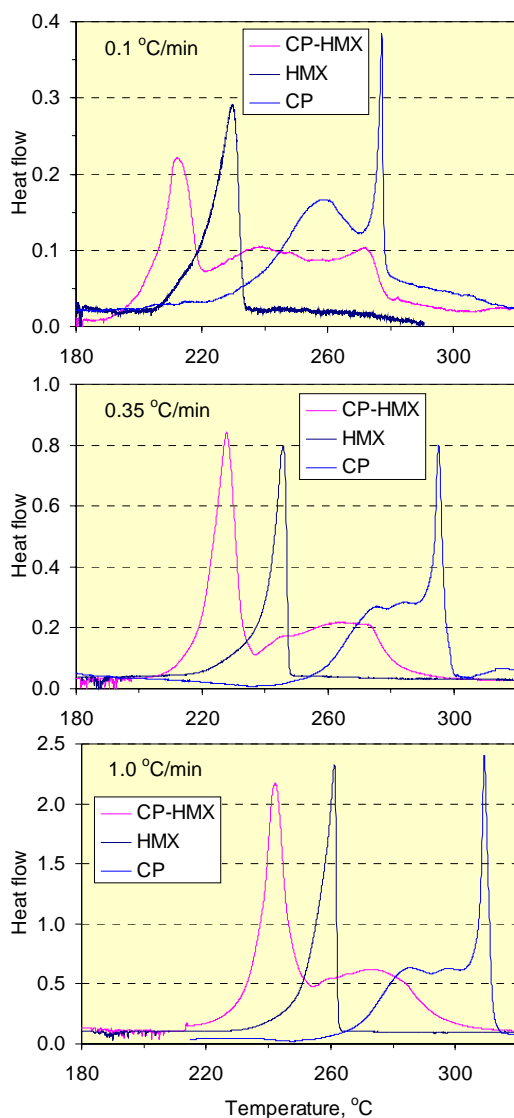


Figure 9. Comparison of DSC reaction profiles of HMX, CP, and CP-HMX mixtures. Note that the endothermic reaction for CP is coincident with the exothermic decomposition of HMX, and it is particularly evident in the profiles at 0.35 °C/min. Even though the CP-HMX mixture decomposes faster than either individually, one should compare the mixture T_{\max} of 240 °C at 1 °C/min to the corresponding values of 180 °C for PETN, 215 °C for RDX, and 275 °C for TNT.

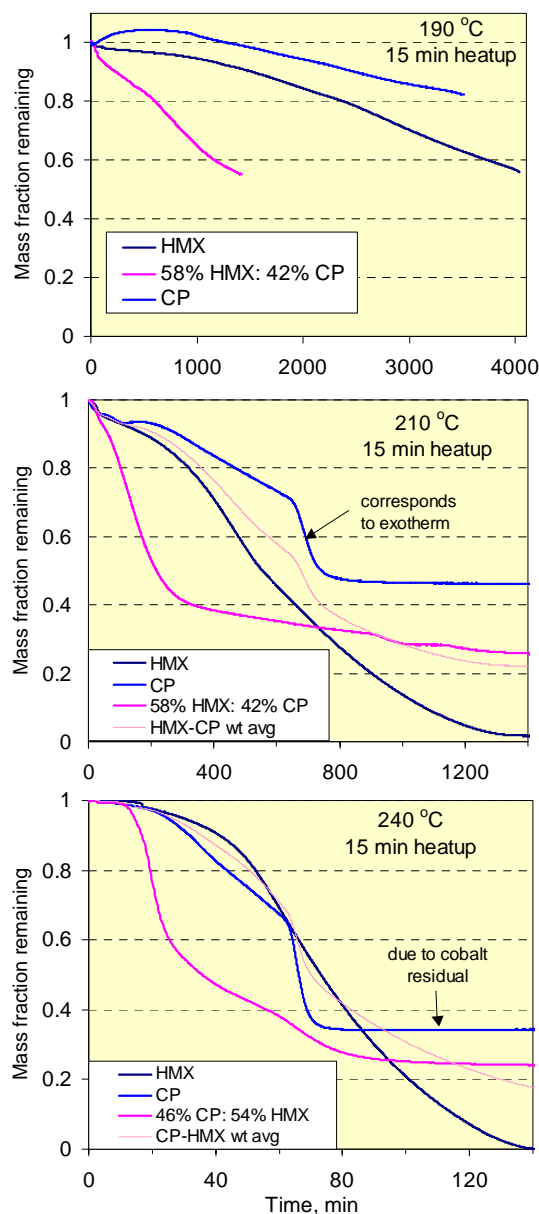


Figure 10. Comparison of isothermal weight loss for neat HMX and CP and mixtures of the two materials. The time for 10% weight loss is accelerated 3-5 times compared to either HMX alone or a weighted average of the two materials independently. The sharp mass loss for corresponds to a sharp exotherm in the simultaneous ΔT signal in the SDT apparatus and probably corresponds to rapid oxidation by perchlorate.

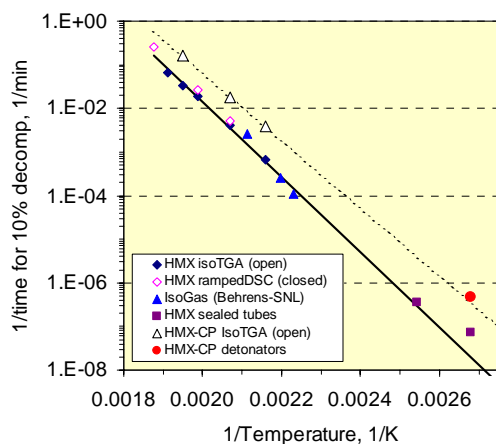


Figure 11. Arrhenius plots for HMX alone, HMX-CP mixtures, and the Sandia aging tests. The enhanced gas yields from the accelerated aging tests are qualitatively consistent with an extrapolation of the high-temperature thermal analysis experiments of CP-HMX mixtures.

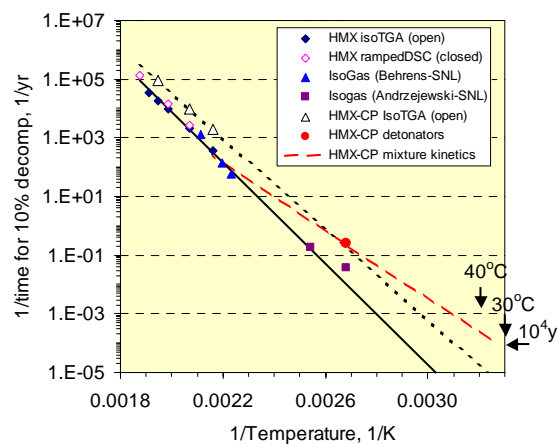


Figure 12. Prediction of mixture lifetimes at 30-40 °C based on an Arrhenius extrapolation of high-temperature and accelerated aging tests. The predicted lifetimes are much greater than required.